

Japan Patent Office  
Kokai Patent Publication No.110570 - 1997, April 28, 1997

Patent Application No. 268360 - 1995  
Date of Application: October 17, 1995

Applicant: 394012706

K. K. Comson Co.

3-41 5-Chome, Asahi Cho, Takamatsu Shi, Kagawa Ken

Inventor: Y. Okamoto

c/o K. K. Comson Co.

3-41 5-Chome, Asahi Cho, Takamatsu Shi, Kagawa Ken

Attorney: H. Aoyama, Patent counsel (and 1 other)

[Title of Invention] Method of making organic fertilizer and the apparatus for it

[Abstract]

[Problem] To provide the organic fertilizer production apparatus that can retain the effective nitrogen of the substance being treated and also can reduce the load on the drainage treatment.

[Means of Solution] The dehydrated sludge cake from the sludge receiving hopper 1 and the sulfuric acid solution from the sulfuric acid tank 2 are mixed by the kneading machine 3 and the pH value of this mixture is made to be below 7 and, by this, the ratio of ammonia NH<sub>3</sub> to the ammonium ion NH<sub>4</sub><sup>+</sup> in the mixture is reduced. Then, the mixture from the said kneading machine 3 and oil are stirred in the stirring and adjusting tank 4 and next the mixture in the stirring adjusting tank 4 is led to the oil heat vacuum type drying apparatus 5 and heating is done in the oil to dry the mixture and, by this, the fertilizer is made. When the drying treatment is conducted by heating in the said oil heat vacuum type drying apparatus 5, there is little ammonia NH<sub>3</sub> in the mixture and so almost no NH<sub>3</sub> is discharged to the vapor phase and so the decrease of amount of ammonia form nitrogen in the fertilizer is prevented and, at the same time, the amount of ammonia form nitrogen transferring to the condensed water, after the evaporation, is reduced.

Fig. 1 (see the figure at the end of text)

[Claims of the Patent]

[Claim 1] The method of making organic fertilizer, the method being characterized by comprising the step of mixing the material to be treated and the acidic solution to bring the pH value of the mixture of the said material to be treated and the said acidic solution to below 7 and the step of drying the said mixture by heating.

[Claim 2] The apparatus for making the organic fertilizer, the apparatus being characterized by comprising

the apparatus for feeding the material to be treated that feeds the material to be treated,  
the acidic solution feed apparatus that feeds the acidic solution,

the mixing apparatus that mixes the said material to be treated from the said apparatus for  
feeding the material to be treated and the said acidic solution from the said acidic solution  
feed apparatus to generate the mixture and bring the PH value of this mixture to below 7,  
and

the drying apparatus for drying the said mixture from the said mixing apparatus by heat-  
ing.

#### [Detailed Description of the Invention]

##### [0001]

[Technological field where the invention belongs] This invention is related to the method  
of making organic fertilizer that makes organic fertilizer from the treated materials of the  
sewage sludge and to the apparatus for it.

##### [0002]

[Existing Technology] The sewage sludge or industrial waste material are generally  
thrown away into the ocean or are used in landfill after burning. However, such disposal  
in ocean or burning contaminate the global environment and causes pollution and so the  
practice is going to be not permissible.

[0003] Thereupon, for the purpose of utilizing the sludge such as the sewage sludge in the  
farmland , the applicant of this application has attempted to make organic fertilizer by  
drying the dehydrated sludge through heat treatment.

##### [0004]

[The Problem that the Invention Intends to Solve] In the above said drying process by  
heat treatment, however, the ammonia form nitrogen in the sludge is easily discharged  
into the vapor phase and the ammonia form nitrogen that stays in the sludge after the  
drying decreases and, consequently, there is the problem that the ammonia form nitrogen  
that is effective as the fertilizer component and is in the form of easy use by the plant can  
not be utilized effectively. ] ←

[0005] Also, the ammonia form nitrogen that is discharged into the vapor phase in the  
drying process of the said superheat treatment transfers to the condensed water after  
evaporation from the sludge and, in order to drain the condensed water into the river  
stream, it is necessary to remove the ammonia form nitrogen that is the rich nutritional  
substance. However, it is difficult to remove the said ammonia form nitrogen from the  
drainage water and so there is the problem of increased load on the water treatment  
facilities. The nitrogen in the said drainage water is an item that was placed as an object  
of regulation recently together with the phosphorus and the technology of removing  
nitrogen from the drainage water is still on the way of being established.

[0006] Thereupon, the objective of this invention is to provide the method of making the organic fertilizer by which the effective nitrogen in the material to be treated can be retained and, at the same time, the amount of ammonia form nitrogen in the drainage water is reduced to lighten the load on the water treatment facilities and to provide the apparatus for it.

[0007]

[The Means for Solving the Problem] To achieve the above said objective, the method of making organic fertilizer and the apparatus for it of Claim 1 are characterized by comprising the step of mixing the material to be treated and the acidic solution to bring the pH value of the mixture of the said material to be treated and the said acidic solution to below 7 and the step of drying the said mixture by heating.

[0008] According to the method of making organic fertilizer of the said Claim 1, the ammonia and ammonium ion are maintaining the equilibrium state of dissociation in the material to be treated such as the sewage sludge and, when the pH value of the material to be treated exceeds 7, by mixing the acidic solution to the material to be treated and bringing the pH value of the mixture to below 7, the dissociation constant becomes large and the ammonium ion increases and, on the other hand, ammonia decreases and so, even when the said mixture is heated and dried, ammonia is not discharged appreciably into the vapor phase. Consequently, the decrease of ammonia form nitrogen in the said material to be treated is prevented and, among the organic nitrogen and the ammonia form nitrogen which are classified as the nitrogen component in the fertilizer, the ammonia form nitrogen that is the form which the plants can use easily can be retained in the treated material after the drying. In the said drying treatment, the ammonia that is discharged from the said mixture to the vapor phase is reduced and the amount of ammonia form nitrogen that transfers to the condensed water after the evaporation from the said mixture is reduced and, consequently, the load on the water treatment facility that removes the ammonia form nitrogen can be lightened.

[0009] Also, the apparatus for making the organic fertilizer of Claim 2 is characterized by comprising

the apparatus for feeding the material to be treated that feeds the material to be treated,

the acidic solution feed apparatus that feeds the acidic solution,

the mixing apparatus that mixes the said material to be treated from the said apparatus for feeding the material to be treated and the said acidic solution from the said acidic solution feed apparatus to generate the mixture and bring the PH value of this mixture to below 7, and

the drying apparatus for drying the said mixture from the said mixing apparatus by heating.

[0010] According to the apparatus for making the organic fertilizer of the above said Claim 2, the material to be treated from the apparatus for feeding the material treated and the acidic solution from the acidic solution feed apparatus are mixed by the said mixing apparatus to generate the mixture and, at the same time, brings the pH value of the mixture to below 7. The mixture from the said mixing apparatus is heated by the drying apparatus and the water contained in the material to be treated is evaporated to conduct the drying. At this time, as the pH value of the said mixture was brought to below 7, the dissociation constant is large and so the ammonium ion increases and, on the other hand, ammonia decreases and, in the drying treatment, ammonia is not discharged appreciably into the vapor phase. Consequently, the decrease of the ammonia form nitrogen in the said material to be treated is prevented and so the ammonia form nitrogen is retained in the treated material after the drying. Also, in the said drying treatment, the ammonia that is discharged from the said mixture to the vapor phase is reduced and the amount of ammonia form nitrogen that transfers to the condensed water after evaporation from the mixture is reduced and, consequently, the load on the water treatment facilities for removing the ammonia form nitrogen is lightened.

[0011]

[Mode of Application of the Invention] In the following, the method of making organic fertilizer and the apparatus for it of this invention are explained in detail by the mode of application illustrated in the figures.

[0012] Fig. 1 is the schematic construction diagram of the apparatus for making the organic fertilizer in the mode of application of this invention. 1 is the sludge receiving hopper as the apparatus for feeding the material to be treated that feeds the dehydrated sludge cake obtained by dehydrating the sewage sludge, 2 is the sulfuric acid tank that stores the sulfuric acid solution for adjusting the pH, 3 is the kneading machine as the mixing apparatus for mixing the dehydrated sludge cake from the said sludge receiving hopper 1 and the sulfuric acid solution from the said sulfuric acid tank 2, 4 is the stirring adjusting tank that stirs the mixture from the said kneading machine 3 and the plant oil (hereinafter, this is called oil) from the oil tank to be described later, 5 is the oil pressure vacuum type drying apparatus as the drying apparatus that dries by heating the said mixture from the said stirring adjusting tank 4 and the oil, 6 is the centrifugal separating machine that separates the sludge that was heat treated in the said oil heat vacuum type drying apparatus 5 and the oil, 7 is the oil tank that stores the oil separated at the said centrifugal separating machine 6 and, at the same time, feeds the oil by the pump 22 to the said stirring adjusting tank 4 and the oil heat vacuum type drying apparatus 5. Also, 8 is the condenser for cooling the vapor from the said oil heat vacuum type drying apparatus 5, 9 is the cooling tower that cools the water being circulated inside the said condenser 8, 10 is the pump for discharging the condensed water inside the said condenser 8, 11 is the drain water tank that stores the water drained from the said condenser 8 through the pump 10, 12 is the water treatment facility for treating the drained water from the said drain water tank 11, 13 is the vacuum pump that reduces the pressure inside the oil heat vacuum type drying apparatus 5 to below the atmospheric pressure.

[0013] In the apparatus for making the organic fertilizer having the above said construction, from the sludge receiving hopper 1, the dehydrated sludge cake is thrown into the kneading machine 3 and, at the same time, from the sulfuric acid tank 2, the sulfuric acid solution is fed by the pump 21 and, by the kneading machine 3, the dehydrated sludge cake and sulfuric acid solution are mixed to adjust the pH value of the mixture to become about 6.5. The mixture from the said kneading machine 3 is led to the stirring adjusting tank 4 and, then the mixture and the oil that is sent by the pump 22 from the oil tank 7 are stirred.

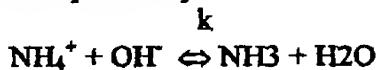
[0014] Next, the mixture of the sludge and oil from the above said stirring and adjusting tank 4 is led to the oil heat vacuum type drying apparatus 5 and the mixture is heated to about 110 deg C under a reduced pressure below the atmospheric pressure. As the result, the water that was contained in the said mixture evaporates and is replaced with the oil and the drying of sludge is conducted.

[0015] Next, from the oil-containing sludge that is discharged from the above said oil heat vacuum type drying apparatus 5, the oil is removed by the centrifugal separating machine 6. The dry sludge that is discharged from the said centrifugal separating machine 6 becomes the organic fertilizer and, on the other hand, the oil that was separated at the centrifugal separating machine 6 is stored in the tank 7 and is reused.

[0016] Also, in the above said oil heat vacuum type drying apparatus 5, the vapor from the oil heat vacuum type drying apparatus 5 is cooled and condensed in the condenser 8 and the condensed water in the condenser 8 is drained to the drain water tank 11 by the pump 10. And the drain water from the said drain water tank 11 is treated by the water treatment facility 12.

[0017] The ammonia contained in the dehydrated sludge cake before the above said treatment maintains the dissociation equilibrium as shown by the following equation.

[Chemical equation 1]



For example, when the OH<sup>-</sup> ion concentration in the said water solution becomes high, i.e. if the pH value of the water solution exceeds 7, the equilibrium of NH<sub>4</sub><sup>+</sup> and ammonia NH<sub>3</sub> in the water solution tilts to the right hand side and the ratio of ammonia NH<sub>3</sub> relative to the ammonium ion NH<sub>4</sub><sup>+</sup> increases. Further, when the water temperature rises, the dissociation constant k increases and the equilibrium tilts to the right hand side and, consequently, the ratio of ammonia NH<sub>3</sub> relative to the ammonium ion NH<sub>4</sub><sup>+</sup> increases. Also, when the said ammonia NH<sub>3</sub> is discharged to the vapor phase and is lost, the equilibrium tilts to the right side to make up the lost ammonia NH<sub>3</sub>. Furthermore, the said ammonia NH<sub>3</sub> has a lower solubility to water than the ammonium ion NH<sub>4</sub><sup>+</sup> and, consequently, when the equilibrium tilts toward the right hand side, i.e. when the ratio of ammonia NH<sub>3</sub> increases, the discharge of ammonia NH<sub>3</sub> to the vapor phase increases.

Consequently, the ratio of ammonia NH<sub>3</sub> goes high by the heat treatment and the amount of discharge of the ammonia form nitrogen to the vapor phase increases.

[0018] Fig. 2 shows the ratio of existence of the ammonia NH<sub>3</sub> and ammonium ion NH<sub>4</sub><sup>+</sup> with respect to the pH value. When the temperature of the water solution is higher, the ratio of ammonium ion NH<sub>4</sub><sup>+</sup> relative to the ammonia NH<sub>3</sub> decreases while the ratio of ammonium ion NH<sub>4</sub><sup>+</sup> relative to the ammonia NH<sub>3</sub> increases when the pH value of the water solution is smaller.

[0019] Table 1 shows the existence ratio of ammonia NH<sub>3</sub> and ammonium ion NH<sub>4</sub><sup>+</sup> at the pH values of 8.5 and 6.0 in Fig. 2. When the sludge at 20 deg C is heated up to 100 deg C at pH of 6.0, the ammonium ion NH<sub>4</sub><sup>+</sup> went from 100 to 96 % and the ammonia NH<sub>3</sub> from 0 % to 4 % and thus they almost did not change while, at the pH value of 8.5, ammonium ion NH<sub>4</sub><sup>+</sup> went from 90 % to 8 % and ammonia NH<sub>3</sub> went from 10 to 92 %, thus showing large changes.

[Table 1]

- A.Concentration
- B.Ratio of NH<sub>4</sub><sup>+</sup>
- C.Ratio of NH<sub>3</sub>

		A	B	C
pH	時間	NH <sub>4</sub> <sup>+</sup> 割合	NH <sub>3</sub> 割合	
8.5	20℃	90%	10%	
	100℃	8%	92%	
6.0	20℃	100%	0%	
	100℃	96%	4%	

Consequently, in the above said apparatus for making the organic fertilizer, by mixing the sulfuric acid solution to the dehydrated sludge cake that is weakly alkaline and adjusting the pH value of the mixture to about 6.5, as is seen in Fig. 2, the ratio of ammonia NH<sub>3</sub> relative to the ammonium ion NH<sub>4</sub><sup>+</sup> went to about less than 10 % at 100 deg C and thus the discharge of ammonia NH<sub>3</sub> to the vapor phase is suppressed at the heat treatment that uses the oil heat vacuum type drying apparatus 5.

[0020] In the following, explanation is given on the results of experiments in the cases of adding and not adding the sulfuric acid solution to the dehydrated sludge cake. Here, the pH value of the mixture of the said dehydrated sludge cake and sulfuric acid solution was made to about 6.5

[0021] For the case of adding sulfuric acid, Table 2 shows the amount of the ammonia form nitrogen in the dehydrated sludge cake before the treatment, the fertilizer after the treatment and in the condensed water (average value in 11 treatments). Also, in Table 2, the amount of ammonia form nitrogen in the condensed water gives the amount of ammonia form nitrogen that transferred to the condensed water at 20 minutes, 35 minutes, 50 minutes and 65 minutes from the initiation of the oil heat vacuum type drying treatment. In table 2, the unit of numerical values is mg/kg.

[Table 2]

- A.Dehydrated sludge cake, a; B.Fertilizer, b;
- C~F.Condensed water, c
- C.After 20 min.; D.35 min.; E.50 min.; F.65 min.

a b	c	d e f			
		20分後	35分後	50分後	65分後
11729	9916	456	281	286	287

For the case of not adding sulfuric acid, Table 3 shows the amount of the ammonia form nitrogen in the dehydrated sludge cake before the treatment, the fertilizer after the treatment and in the condensed water (average value in 12 treatments). Also, in Table 3, the amount of ammonia form nitrogen in the condensed water gives the amount of ammonia form nitrogen that transferred to the condensed water at 20 minutes, 35 minutes, 50 minutes and 65 minutes from the initiation of the oil heat vacuum type drying treatment. In table 3, the unit of numerical values is mg/kg.

[Table 3]

A. Dehydrated sludge cake, d; B. Fertilizer, e;

C~F. Condensed water, f

C. After 20 min.; D. 35 min.; E. 50 min.; F. 65 min.

脱水汚泥ケーキ d	肥料 e	凝縮水 f			
		20分後	35分後	50分後	65分後
12189	4676	1615	1417	1013	770

Based on Table 2 and Table 3 shown above, the changes in the ammonia form nitrogen of the dehydrated sludge cake and the fertilizer after the treatments for the cases of adding and not adding sulfuric acid are shown in Fig. 3. As is seen from the changes in the ammonia form nitrogen shown in Fig. 3, the decrease of ammonia form nitrogen in the fertilizer is greatly suppressed in the case of adding the sulfuric acid in comparison to the case of not adding the sulfuric acid.

[0022] Also, Table 4 shows the retention ratio of the ammonia form nitrogen in the fertilizer that was determined from Table 2 and Table 3 and Table 5 shows the discharge ratio of ammonia form nitrogen to the condensed water that was determined from Table 2 and Table 3.

[表4]

[Table 4], [Table 5]

1. 水酸化物添加時 b / a × 100	85%
2. 水酸化物添加時 c / e × 100	33%

1. Case of adding sulfuric acid

2. Case of not adding sulfuric acid

C. After 20 min.; D. 35 min.;  
E. 50 min.; F. 65 min.

時間 c / a × 100	凝縮水 f / d × 100			
	20分後	35分後	50分後	65分後
1. 水酸化物添加時 c / a × 100	4%	2%	2%	3%
2. 水酸化物添加時 f / d × 100	13%	12%	8%	6%

Based on Table 5 shown above, the change of the amount of ammonium form nitrogen is shown in Fig. 4 as the function of elapsed time from the initiation of the oil heat vacuum type drying treatment. From the change of the amount of ammonia form nitrogen shown in Fig. 4, it is seen that, in the case of adding sulfuric acid, the discharge of ammonia form nitrogen is small regardless of the elapsed time.

[0023] In this way, by mixing sulfuric acid solution to the said dehydrated sludge cake and making the pH value of the mixture to about 6.5, the dissociation constant becomes large and the ratio of ammonia NH<sub>3</sub> relative to the ammonium ion NH<sub>4</sub><sup>+</sup> decreases. Consequently, even when the mixture of the said dehydrated sludge cake and the sulfuric acid solution and oil is heat-treated by the oil heat vacuum type drying apparatus 5, the amount of discharge of the ammonia NH<sub>3</sub> to the vapor phase decreases and so it becomes possible to retain, in the dry fertilizer that was de-oiled after the heat treatment, the

ammonia form nitrogen that is of the form which can be utilized easily by the plants, among the organic nitrogen and ammonia form nitrogen that are distinguished as the nitrogen components in the fertilizer. Also, in the heat treatment by the said oil heat vacuum type drying apparatus 5, the ammonia that is discharged from the mixture to the vapor phase decreases and the amount of ammonia form nitrogen in the condensed water after the evaporation decreases and, consequently, the load on the water treatment facility 12 that removes the ammonia form nitrogen can be reduced.

[0024] Also, in the said oil heat vacuum type drying apparatus 5, the said mixture is heated in the oil and, therefore, the water in the mixture is replaced with oil and the moisture content in the sludge can be evaporated with a good efficiency.

[0025] Also, by the above said oil heat vacuum type drying apparatus 5, the said mixture is heated under a reduced pressure below the atmospheric air pressure and, therefore, the evaporation of the moisture content in the sludge is accelerated at a relatively low temperature. Also, as the organic substances in the sludge are not burned, the organic fertilizer having rich nutrition of good quality can be made.

[0026] In the above described mode of application, in the oil heat vacuum type drying apparatus 5 as a drying apparatus, the sludge that is the material to be treated is dried by heating in oil but the heating and drying system by a drying apparatus is not limited to this and it can be the convective heat transfer (hot air) drying, conductive heat transfer drying, radiative transfer drying, etc.

[0027] Also, in the above described mode of application, the dehydrated sludge cake and sulfuric acid solution were mixed and the pH value of this mixture was adjusted to about 6.5. But, as for the pH value of this mixture, it can be made to a suitable value below 7 at which the ratio of ammonia NH<sub>3</sub> relative to the ammonium ion NH<sub>4</sub><sup>+</sup> is less than about 20 % at 100 deg C.

[0028] Also, in the above described mode of application, to the sludge that is the material to be treated, the sulfuric acid solution was mixed as the acidic solution but the acidic solution is not limited to this and one can use any of the inorganic acid or organic acid (for example citric acid).

[0029] Also, in the above described mode of application, as the material to be treated, the sewage sludge was treated but the material to be treated is not limited to this and, naturally, it can be the raw refuse, excreta and industrial waste material.

#### [0030]

[Effectiveness of the Invention] As is clear from the above, in the method of making the organic fertilizer of the invention of Claim 1, the material to be treated and acidic solution are mixed to make the pH value of the mixture of the said material to be treated and acidic solution to be below 7 and, consequently, the dissociation constant of ammonia and ammonium ion at the dissociation equilibrium state in the mixture becomes large and the ammonium ion increases and, on the other hand, ammonia decreases. And, when the

said mixture is heated, the ammonia that is discharged to the vapor phase is reduced and so the reduction of ammonia in the mixture is prevented. Consequently, even when the said mixture is dried by heating, ammonia is not discharged to the vapor phase appreciably and so the decrease of ammonia form nitrogen is prevented and the effective nitrogen is retained in the treated material after drying. Also, in the drying treatment, the amount of ammonia form nitrogen contained in the condensed water after the evaporation from the mixture is reduced and so the load on the water treatment facility for removal of the ammonia form nitrogen can be lightened.

[0031] Also, in the apparatus for making the organic fertilizer of the invention of Claim 2, the material to be treated coming from the feed apparatus of the material to be treated and the acidic solution from the acidic solution feed apparatus are mixed by the mixing apparatus to generate the mixture and, at the same time, the pH value of the mixture is made to be less than 7 and, after this, the mixture from the said mixing apparatus is heated by the cooker and the water contained in the material to be treated is evaporated to make the organic fertilizer. At this time, as the pH value of the said mixture is below 7, the dissociation constant has become large and the ammonium ion increases while the ammonia decreases and the amount of ammonia that is discharged to the vapor phase at the drying treatment is reduced. Consequently, the decrease of ammonia form nitrogen in the mixture at the time of said heat treatment is prevented and the effective nitrogen can be retained in the fertilizer after the drying. Also, in the said drying treatment, the amount of ammonia form nitrogen that transfers to the condensed water after the evaporation from the mixture is small and so the load on the water treatment facility for removing the ammonia form nitrogen can be lightened.

#### [Brief Description of the Figures]

[Fig. 1] is the schematic construction diagram of the apparatus for making the organic fertilizer of the mode of application of the invention.

[Fig. 2] is the diagram showing the ratio of existence of ammonia and ammonium ion as the function of pH value.

[Fig. 3] shows the amount of ammonia form nitrogen in the cases of adding and not adding sulfuric acid based on the experimental results with the apparatus for making the organic fertilizer of the above said mode of application

[Fig. 4] shows the amount of ammonia form nitrogen in the condensed water as the function of elapsed time from the initiation of the oil heat vacuum type drying treatment based on the experimental results by the above said apparatus for making organic fertilizer.

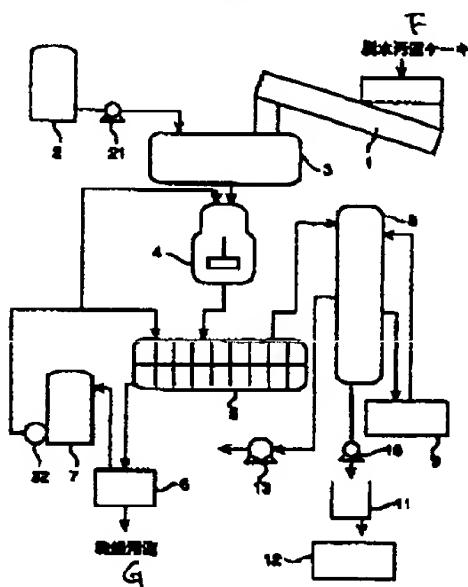
#### [Description of the codes]

1—Sludge receiving hopper, 2---Sulfuric acid tank, 3---Kneading machine, 4---Stirring adjusting tank, 5---Oil heat vacuum type drying apparatus, 6---Centrifugal separating

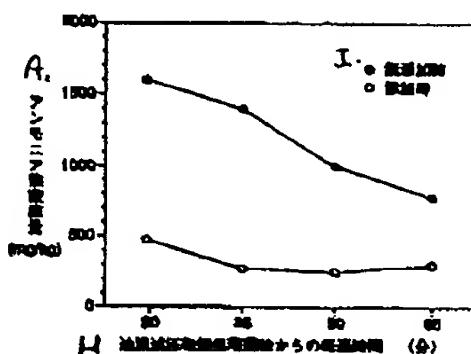
machine, 7—Oil tank, 8—Condenser, 9—Cooling tower, 10, 21, 22--- Pumps, 11—Drain water tank, 12 — Water treatment facility

### Figures.

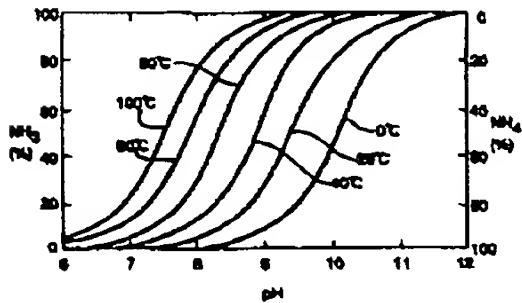
[図1]



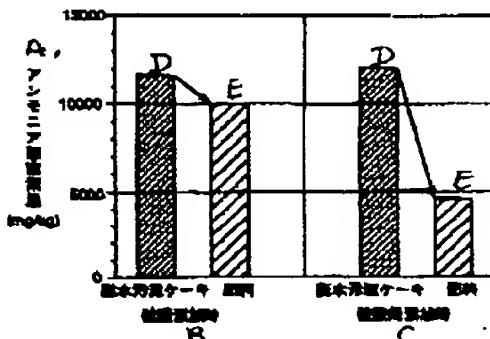
[図4]



[図2]



[図3]



A. Amount of ammonia form nitrogen (mg/ kg); B. Case of adding sulfuric acid; C. Case of not adding sulfuric acid; D. Dehydrated sludge cake; E. Fertilizer; F. Dehydrated sludge cake; G. Dry sludge; H. Elapsed time from the initiation of oil heat vacuum type drying treatment; I. Black dot: Case of no addition; White circle: Case of addition